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nitroso-derivative of phtalimidine
with potassium hydroxide

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**THE DECOMPOSITION REACTION OF THE
NITROSO-DERIVATIVE OF PHTALIMIDINE
WITH POTASSIUM HYDROXIDE**

BY

JAMES AUSTIN COSS

B. S. Illinois Wesleyan University, 1903

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

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June 1,

1910.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

James Austin Coss

ENTITLED The Decomposition Reaction of the Nitroso-derivative of
Phtalimidine with Potassium Hydroxide.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF

Master of Science

W. A. Coss.

In Charge of Major Work

W. A. Coss.

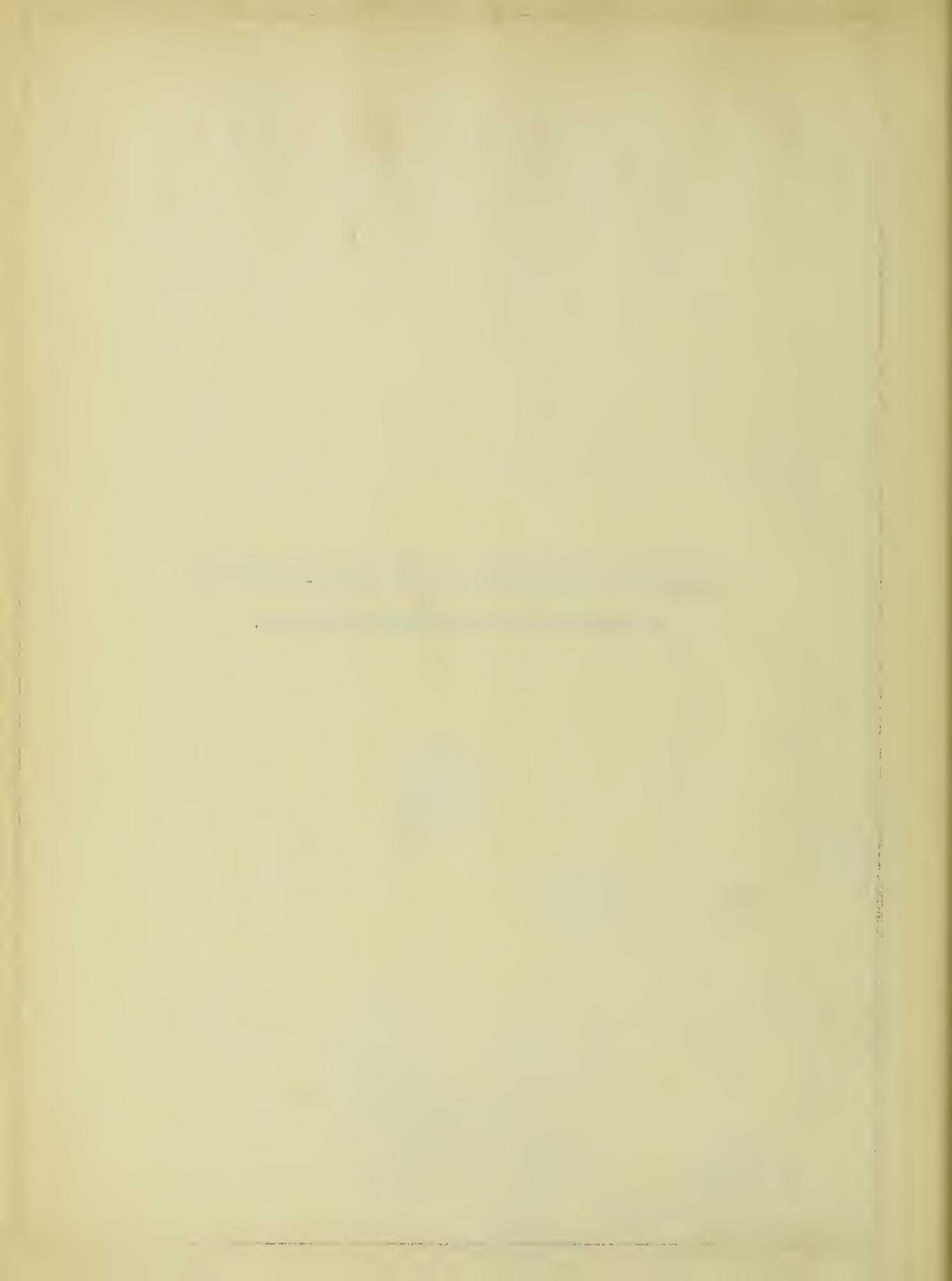
Head of Department

Recommendation concurred in:

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Final Examination

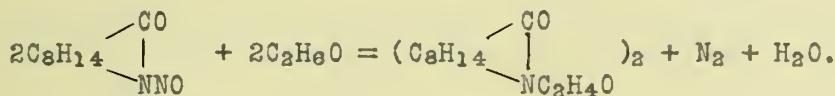
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THE DECOMPOSITION REACTION OF THE NITROSO-DERIVATIVE
OF PHTALIMIDINE WITH POTASSIUM HYDROXIDE.



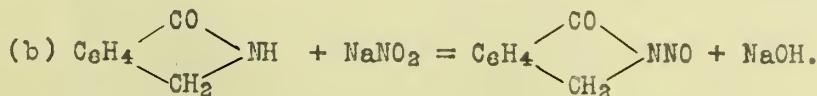
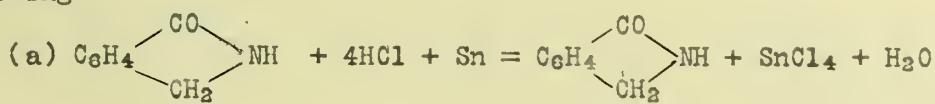
This work is a continuation of some work done by Professor William A. Noyes and René¹ M. Taveau¹. It was hoped that a general method for the formation of double molecular substances from nitroso compounds would be found and their structure determined.

They decomposed the nitroso compound obtained from amino lauronic anhydride, $\text{C}_8\text{H}_{14}\begin{array}{c} \text{CO} \\ | \\ \text{NNO} \end{array}$, in the presence of an excess of ethyl alcohol by means of the calculated amount of sodium hydroxide and obtained a 25 per cent. yield of a product represented by the following formula $(\text{C}_8\text{H}_{14}\begin{array}{c} \text{CO} \\ | \\ \text{NC}_2\text{H}_4\text{O} \end{array})_2$. The reaction was represented by this formula:



Preparation of the Nitroso-derivative of Phtalimidine.

Phtalimidine was prepared by the method of Graebe². 25 grams of finely powdered phtalimide was warmed with 40 grams of granulated tin in 40 cc. of water. Then 125 cc. of hydrochloric acid (sp. gr. 1.19) were added drop by drop and the solution was heated on a water-bath until all of the tin and phtalimide dissolved. After thoroughly cooling the solution the tin was removed by precipitation with zinc. On adding the calculated amount of sodium nitrite very fine yellow needle crystals precipitated at once, but the solution was allowed to stand in contact with the crystals for one hour to complete the precipitation. After recrystallization from alcohol the substance melted at 154° . Yield 16.5 grams. The reaction equations may be represented by the following:

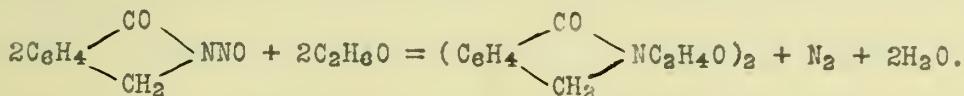




Decomposition of the Nitroso Compound.

To 8 grams of the nitroso compound dissolved in 30 cc. of ethyl alcohol 2 grams of potassium hydroxide dissolved in 20 cc. of ethyl alcohol was slowly added, the solution being cooled in an ice mixture. At the end of the reaction a bright wine colored solution remained, from which a heavy red oil separated on adding water. After the oil had been extracted with ether the washings and original solution gave clear white plate crystals which redissolved at room temperature on standing over night. This precipitate was not studied farther.

The following formula represents the decomposition of the nitroso compound.



The compound $(\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \\ \text{CH}_2 \end{array} \text{NC}_2\text{H}_4\text{O})_2$ was separated by extracting with ether after the alcohol had been evaporated off. A greenish yellow oil remained after the ether was evaporated. The oil was found to be insoluble in water and alcohol but readily soluble in ether, ligroin and benzene. In a solution of benzene with a drop or two of water added beautiful yellow needle crystals separated slowly after standing about three days. Melting point 145° .

A molecular weight determination by Raoult's method; 0.1120 grams of the compound dissolved in 44 grams of benzene with a freezing point depression of 0.38° ; gave 324 for the molecular weight. The calculated molecular weight for $(\text{C}_{10}\text{H}_{10}\text{NO}_2)_2$ is 352. The result was not satisfactory but the agreement is close enough to show the compound is dimolecular.

A single analysis showed the following:

Substance	Theory	Found
Carbon	68.18 per cent.	68.20 per cent.
Hydrogen	5.68 " "	6.03 " "
Oxygen	18.19 " "	
Nitrogen	7.95 " "	

On standing three months dissolved in benzene 5 grams of the above substance gave a fine grained white precipitate which was insoluble in ether, alcohol and benzene in cold solutions but was soluble in large excess of boiling benzene. The melting point was found to be 242° . This compound was not investigated farther. The benzene was evaporated from the original solution and the oily product remaining was subjected to fractional distillation:

Fraction	boiling point	pressure
No. 1	160°	20 m.m.
No. 2	270°	20 m.m.

Fraction No. 1 was a clear oily substance from which white plate crystals separated on cooling. Melting point 70° . Boiling point 283.5° . These properties are in substantial agreement with phtalide which has a melting point 73° and boiling point 290° . The clear oil remaining after the crystals were separated could not be made to crystallize and did not contain a trace of the nitrogen as was shown by fusing it with metallic sodium, dissolving in dilute ferrous sulphate and adding hydrochloric acid. Boiling point 260° . Molecular weight determinations by the Raoult method gave; 0.3735 gram in 11.95 grams of benzene, depression 0.80° , 0.7057 gram in 12.28 grams of benzene, depression 1.50° ; molecular weights 190 and 188 respectively. With glacial acetic acid as the solvent; 0.7420 gram in 28 grams of acetic acid, depression 0.49° ; 0.4300 gram in 12.89 grams of acetic acid, depression 0.63; the results gave respectively 210 and 205 as the molecular weight.

Combustion analysis gave the following:

	I	II	III	IV
Weight	Per cent.	Weight	Per cent.	Weight
Carbon	.4842 g. = 67.72	.2400 g. = 67.30	.2865 g. = 67.60	.4086 g. = 67.29
Hydrogen	.0508 " = 7.10	.0255 " = 7.16	.0308 " = 7.27	.0412 " = 6.78
Oxygen	.1740 " = 23.76	.0911 " = 25.54	.1065 " = 25.12	.1574 " = 25.92

These results correspond closely to the formula $C_{10}H_{12}O_3$ although the hydrogen is a little high the factors for the above formula being 66.7 per cent., 6.7 per cent. and 26.6 per cent. respectively with a molecular weight of 180.

The speed of the decomposition reaction seemed to indicate that the potassium hydroxide acted as a catalytic agent only. To test this inference a normal solution of potassium in absolute alcohol was prepared by putting the weighed amount of pure dry metallic potassium in the alcohol. The absolute alcohol was prepared by twice distilling ordinary 95 per cent. alcohol from quick lime and freshly fused copper sulphate. One drop of the normal potassium solution was added to 25 grams of the nitroso compound in 50 cc. of alcohol. The mixture was allowed to boil by the heat of reaction. It was found necessary to cool the solution frequently to keep it from boiling over. The solution was alkaline at the end of the reaction and additions of more of the potassium solution had no effect on it. No attempt was made to collect the evolved nitrogen when the potassium solution was used, but subsequent tests showed that all the nitrogen was evolved as no nitrogen could be found in the products. An apparatus was arranged to collect the gas evolved from .5 gram of the nitroso compound in alcoholic solution when one drop of normal sodium hydroxide was added. At 25° and barometric pressure of 747 m.m. 46.5 cc. of nitrogen was collected, or 42 cc. corrected for temperature and pressure. Calculated for the nitrogen evolved:

$$162 : 22.4 :: 0.5 : x, x = .0692 \text{ liter or } 69.2 \text{ cc.}$$

For one-half of the nitrogen:

$$324 : 22.4 :: 0.5 : x, x = .0346 \text{ liter or } 34.6 \text{ cc.}$$

The molecular weight of the nitroso compound as used in the above proportions is 162. The difference 7.4 cc. between the theory and volume found could not be accounted for except on the supposition that some of the compound must have

liberated all of its nitrogen. The solution was found to be alkaline at the end of the reaction. These results showed conclusively that sodium and potassium acted catalytically. The oil which separated on adding water was extracted with ether, dried over calcium chloride and subjected to fractional distillation with results similar to the compound obtained from standing in benzene.

Fraction	boiling point	pressure
No. 1	175°	30 m.m.
No. 2	275 to 280°	30 m.m.

Fraction No. 1 came over at fairly constant temperature but on cooling 7 grams of phtalide separated from the clear oil. Redistilling the oil 5 grams of the pure product was obtained. Fraction No. 2 was a heavy yellow oil which did not have a definite boiling point but increased as the distillation progressed. When the heating was discontinued a black gummy mass remained in the distilling flask.

One gram of the clear oil reduced with hydriodic acid (sp. gr. 1.5) by heating in a sealed tube for ten hours gave 0.0845 gram pure white crystals. Melting point 105°. The entire product above 0.0845 gram was dissolved in water and titrated with sodium hydroxide (normal factor 0.09) with phenolphthalein as indicator; 7.71 cc. sodium hydroxide was required to neutralize the acid. 7.71 cc. N/.09 sodium hydroxide is equal to .704 cc. normal.

$\frac{.0845}{.704} = .12$ equivalent of acid. Ortho-toluic acid which has a melting point of 104° molecular weight 136 agrees substantially with the above compound.

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A second reduction was made with two grams of the oil with hydriodic acid, the heating at 130° being continued for two hours. The more volatile portion of the solution was distilled off rapidly on a metal bath and collected in a flask which was kept cold by a freezing mixture. 2 cc. of the liquid was obtained which had the characteristic odor of ethyl iodide. Boiling point 73°.

Oxidation of the Oils with Nitric Acid.

0.5 gram of the oil was heated 12 hours with concentrated nitric acid. A white crystalline precipitate was obtained on adding water to the cooled solution. Melting point 207° but when cooled and remelted 128°. Yield 0.25 gram.

0.2296 gram of the above compound was made up to 53.36 cc. of solution or N/20 on the basis of a bibasic acid. 1 cc. = $\frac{0.2296}{53.36} = 0.00429$ gram. The above solution was then titrated with a N/.0894 sodium hydroxide solution with the following result:

8.55 cc. solution required 4.98 cc. NaOH solution, or in grams 8.55 cc. x

$0.00429 = 0.03668$ gram. $\frac{36.68}{8.3} = 4.42$ cc. calculated N/10 NaOH. 4.98×0.894
 $= 4.45$ cc. N/10 NaOH required.

Saponification of the Oil with Potassium Hydroxide.

3.6 grams of the oil dissolved in alcohol was heated with potassium hydroxide (1 part to 1 part water) for twelve hours on a steam bath. After the alcohol was evaporated off the solution was neutralized with hydrochloric acid. A white precipitate was obtained which after purifying by recrystallization from hot water gave a melting point of 83° .

This product reduced with hydriodic acid gave ethyl iodide and orthotoluic acid.

An analysis of the saponification product gave the following:

Carbon $0.1925 = 63.7$ per cent. $\div 12 = 5.3$

Hydrogen $0.0207 = 6.85$ " " $\div 1 = 6.85$

Oxygen $0.0890 = 29.45$ " " $\div 16 = 1.83$

Taking these results with the titration below the formula is $C_{10}H_{12}O_2$ or graphically represented $C_6H_4\begin{array}{c} \text{O} \\ \diagup \\ \text{CH}_3 \end{array} - \text{O} - C_2H_5$

Titration with Potassium Hydroxide.

$N/0.0709 \cdot 0.0683$ gram required 5.82 cc. for neutralization. $5.83 \times 0.709 = 4.12$ cc. N/10. $\frac{0.0683}{4.12} = 0.0165$ for 1 cc. N/10 potassium hydroxide. Hence the molecular weight is 165. Calculated for $C_{10}H_{12}O_2$ the molecular weight is 164.

0.7180 gram of the oil converted into ethyl iodide and this as a vapor passed through silver nitrate formed 0.8920 gram of silver iodide. This indicates that there is only one methyl group in the molecule. But a combustion of the oil that had been twice washed with hot potassium hydroxide to get rid of phtalid gave:

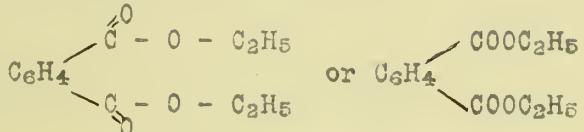
Weight of oil 0.3240 gram.

Carbon 0.2104 = 65 per cent. \div 12 = 5.416

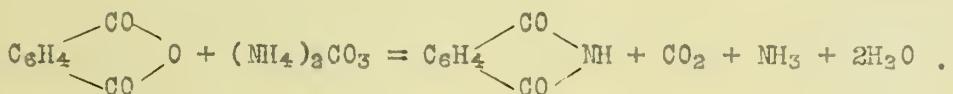
Hydrogen 0.0249 = 7.37 " \div 1 = 7.370

Oxygen 0.0887 = 27.63 " \div 16 = 1.726

which gives $C_{12}H_{14}O_4$ for the formula or



During the progress of this work it was found necessary to prepare phthalimide from phthalic anhydride. The method given by Dunlap¹ was modified, on the suggestion of Professor Noyes, ammonium carbonate being used instead of urea. 25 grams of finely powdered phthalic anhydride was mixed with powdered ammonium carbonate and heated on a metal bath to 300°. At this temperature the substance became liquid with a vigorous evolution of ammonia and carbon dioxide. After heating for about ten minutes or until the gases were no longer evolved the hot liquid was poured into a dish and powdered as soon as cool. A yield of 22 grams was obtained after recrystallizing from hot water. The reaction is represented by this formula:







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